Studies on Acetylene and its Derivatives. (XIII) Preparation of Caprolactam from Propargyl Alcohol. (1)

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19. Studies on Acetylene and its Derivatives. (XIII)

Preparation of Caprolactam from Propargyl Alcohol. (1)

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According to the following scheme, we have been trying the preparation of caprolactam.

$$2CH\equiv C\cdot CH_2OH + 1/2O_2 \xrightarrow[NH_4Cl]{Cu_2Cl_2} HOCH_2-C\equiv C-C\equiv C\cdot CH_2OH$$

$$\xrightarrow[+4H_2]{\text{Raney Ni}} HO(CH_2)_6OH \xrightarrow[-2H_2]{\text{Cu, Cr}} \text{(cyclic ether)} \xrightarrow{NH_3} \text{(lactam)}$$

In this paper, the oxidative coupling of propargyl alcohol to hexadiynediol, using air or oxygen and a cuprous salt as catalyst, and its hydrogenation to hexanediol are described.

A shaking stainless steel autoclave of 300 c.c. capacity was filled with a mixture of 60g. H_2O, 19g. NH_4Cl, 6g. Cu_2Cl_2 and pure propargyl alcohol. Air or oxygen was pressed to 10~20 atm. After the reaction was over, the contents of the autoclave were filtered, the solid washed with a possible minimum amout of water and dissolved in 10 times methanol. Removing the insoluble materials, the methanol solution of hexadiynediol was hydrogenated with 40 atm. hydrogen at 10~20°, in the presence of Ranney nickel catalyst. The anti-catalytic action of copper ions could be eliminated by addition of a small amount of zinc dust.

The yields of hexanediol boiling at 110°/4mm., melting at 40~41° were 50~60 % of the theoretical amounts based on the propargyl alcohol used. Using pure hexadiynediol melting at 112° which was recrystallized from methanol or water, 94 % yield of hexanediol was obtained.

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20. On the Action of Papain Enzyme. (VII)

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It was formerly reported that Rongalite makes papain enzyme active in protein decomposition.